

ZAPADNYUK, V.I.; ZAKHARIYA, Ye.I.

Desensitizing effects of rhodanine derivatives. Farm.i toks.  
24 no.1:33-36 Ja-F '61. (MIRA 14:5)

1. Kafedra farmakologii (zav. - prof. A.A.Gavrilyuk) i kafedra  
patologicheskoy fiziologii (zav. - prof. I.I.Fedorov) L'vovskogo  
gosudarstvennogo meditsinskogo instituta.  
(THIAZOLES RHODANINE) (ALLERGY)

ZAKHARIYA, Ye.A.; ZAPADNYUK, V.I. (L'vov)

Spasmolytic effect of novocains. Pat. fiziol. i eksp. terap. 3 no.3:  
77 My-Je '59. (MIRA 12:7)

1. Iz kafedry patofiziologii (zav. - prof. I.I. Fedorov) i kafedry  
farmakologii (zav. - prof. A.A. Gavrilyuk) L'vovskogo meditsinskogo  
instituta.

(PROCAINE, eff.

on exper. convulsions (Rus))

(CONVULSIONS, exper.

eff. of procaine (Rus))

ZAKHARIYA, Ye. A.

"The Effect of Strong Stimulation and Parabiologic Inhibition on the Emergence and Course of Inflammation (Experimental Investigation)." Cand Med Sci, L'vov State Medical Inst, L'vov, 1953. (RZhEiol, No 4, Oct 54)

Survey of Scientific and Technical Dissertations Defended at USSR Higher Educational Institutions (10)

SO: Sum. No. 481, 5 May 55

ZAKHARIYA, Ye.A.; FEDOROV, I.I.

Disintoxicating effect of sodium lactate in poisoning with narcosis.  
Vrach.delo no.2:71-75 F '63. (MIRA 16:5)

1. Kafedra patologicheskoy fiziologii (zav. - prof. I.I. Fedorov)  
Lvovskogo meditsinskogo instituta.  
(NARCOTICS) (SODIUM LACTATE)

ZAKHARLYA, Ye.A.; ZAPADNYUK, V.I.

Reproduction of audiogenic convulsions after the preliminary administration of pyranidone to animals. Biol. zhur. otd. i med. 58 no.8:82-84 Ag 64. (MIRA 18 3)

1. Kafedra patologicheskoy fiziologii (zav. - dotsent V.P. Bez-uglov) i kafedra farmakologii (zav. - prof. A.A. Gavrilyuk) L'vovskogo meditsinskogo instituta. Submitted April 10, 1962.

ZAKHARIYA, Ye.A.

Method of inducing audiogenic convulsions. Pat. fiziol. i  
eksp. terap. 9 no.3:78-79 My-Je '65. (MIRA 18:9)

1. Kafedra patologicheskoy fiziologii (zav.- dotsent V.P.  
Bezuglov) L'vovskogo meditsinskogo instituta.

ZAPADNYUK, Ignat'y Pavlovich, prof.; ZAPADNYIK, Vitaliy Ignat'yevich,  
kand. med. nauk; ZAKHARIYA, Yekaterina Andreyevna, , kand.  
med. nauk; FEDOROV, I.I., prof., doktor med. nauk, red.;  
ZAPOL'SKAYA, A.A., tekhn. red.

[Laboratory animals, their breeding, keeping, and use in  
experiments] Laboratornye zhivotnye, ikh razvedenie, soder-  
zhanie i ispol'zovanie v eksperimente; s predisloviem i pod  
red. I.I.Fedorova. Kiev, Gosmedizdat USSR, 1962. 349 p.  
(MIRA 16:7)

(LABORATORY ANIMALS)

ZAKHARIYEV, B., kand.med. nauk (Sofiya)

Treatment of psoriasis. Vest. derm. i ven. 37 no. 10:76-77  
O '63. (MIRA 17:9)



ITEM NO. 1, SECRET, A 1, ZAKLON P.C.

Capacity indicator for radiochemical analysis. Source 1, 2.  
From 10-10-1991. Je 10.

1. H. M. Vorkov, Radiochemical analysis of the results of the  
analysis. Summary of the results of the analysis.

ABRASHEV, G.P.; RADEV, R.I.; TSENKOV, TS.G.; DIMOV, N.D.; ZAKHARIYEV, I.TS.;  
PENCHEV, S.P.; TSONEV, M.D.; SHADEL'SKIY, G.A.

Crude oil of the Dolni Dubnik field. Khim i tekhn. topl. i masel 8  
no.11:24-30 N '63. (MIRA 16:12)

ZAKHARIYEV, N.; BAKRACHEV, N.; POPOV, I. (Bolgariya)

Acute poisoning by explosion gases. Gig. truda i prof. zab.  
4 no.12:45-47 D '60. (MIRA 15:3)

1. Dimitrovskaya bel'nitsa dlya shakhterov.  
(MINE GASES—TOXICOLOGY)  
(ELASTING—HYGIENIC ASPECTS)

GEGUHADZE, R.A.; ZAKHARIYEV, A.I.

Making coke briquets from weakly caking lean Bulgarian coals.  
Trudy IOI 20:155-158 '63. (MIRA 17:8)

ZAKHARIYEV, V.I.; GODEV, N.G.

Numerical scheme of a forecast by a two-level model of the atmosphere on the basis of the solution of the complete system of hydrothermodynamic equations. Trudy MTS no.6:25-32 '65. (MIRA 18:12)

MILENKOV, Kh.R.; KIRIN, I.; AGOPYAN, K.; ZAKHARIYEVA, Z.

Influence of hemp dust on some body functions. Gig. i san. 26 no.4:  
25-32 Ap '61. (MIRA 15:5)

1. Iz kafedr patologicheskoy anatomii, patologicheskoy fiziologii  
i fiziologii Meditsinskogo instituta imeni I.P.Pavlova, Plovdiv,  
Bolgariya.

(HEMP...PHYSIOLOGICAL EFFECT)

ZAKHARIYEVA, M. [Zakharieva, M.K.], d-r; SOLOMONOVA, K.

Standardization of the tetanus anatoxin. Pt. 1. Trudy epidemiol  
mikrobiol 8:83-89 '61 [publ. '62].

1. Chlen Redaktsionnoy kollegii, "Trudy Nauchno-issledovatel's-  
skogo instituta epidemiologii i mikrobiologii" (for Zakharieva).

DAVITASHVILI, L.Sh., akademik; ZAKHARIYEVA-KOVACHEVA, Kr.

Origin of the "Stone Forest" near Varna, Bulgaria. Soob. AN Gruz.  
SSR 30 no.4:441-446 Ap '63. (MIRA 17:9)

1. Institut paleobiologii AN GruzSSR, Tbilisi. 2. Akademiya  
nauk Gruzinskoy SSR (for Davitashvili).



DAVITASHVILI, L.Sh., prof.; ZAKHARIYEVA-KOVACHEVA, K.R.

Mystery of a "stone forest" in Bulgaria. Priroda 52 no.9:  
90-91 '63. (MIRA 16:11)

1. Institut paleobiologii AN GruzSSR (for Davitashvili).
2. Sofiyskiy gosudarstvennyy universitet, kafedra paleontologii  
(for Zakhariyeva-Kovacheva).

ZAKHARIYEV-KOVACHEVA, Kr.

One more "petrified forest" in the People's Republic of Bulgaria.  
Soob. AN Gruz. SSR 36 no.1:123-126 O '64.

(MIRA 18:3)

1. Sofiyskiy gosudarstvennyy universitet, Bolgariya. Submitted  
July 10, 1964.

ZAKHARIYEVA-KOVACHEVA, Kr.

Second "stone forest" of Bulgaria. Priroda 53 no.10:  
114-115 '64.

(MIRA 17:11)

1. Sofiyskiy universitet, Bolgariya.

ZAKHARKEVICH, I.P.; BELEN'KIY, A. Yu.

Mondor's disease in general furunculosis and axillary hidradenitis. Zdrav. Bel. 9 no.7:85 J1'63 (MIRA 17:4)

1. Iz Kostyukovichskoy rayonnoy bol'nitsy (glavnyy vrach V.K. Polevtsov).

ACC NR: AP6036102

SOURCE CODE: UR/0256/66/000/011/0067/0070

AUTHOR: Zakharkin, D. F. (Engineer, Lt. Col.)

ORG: none

TITLE: Amplitude velocity curve of a moving target selector

SOURCE: Vestnik protivovozhushnoy oborony, no. 11, 1966, 67-70

TOPIC TAGS: radar signal, moving target, radar tracking, computer application

ABSTRACT: Method of differentiation between radar signals reflected by stationary and moving targets is being discussed under the conditions which occur when the two coincide. Such a situation arises in the case of "blind velocities," i.e., such radial velocities of moving targets with respect to the receiving stations at which the reflected signals are in constant phase relationships and, therefore, are suppressed by the computer of the moving target selector in the same manner as the signals reflected by stationary targets. The MTS amplitude-velocity curves are useful in mathematical calculations leading to the isolation of the signals derived from MTS. In order to eliminate the "blind velocities" within a sufficiently wide range of Doppler frequencies a multiple sequential reading of the received signals is employed simultaneously with the alternating frequency of the sounding radar impulses. In this manner the first segment of the amplitude-velocity curve, which corresponds to the spectrum of the Doppler frequency of the interference, is sufficiently steep,

Card 1/2

ACC NR: AP6036102

and the operational range of the target's velocities is sufficiently wide to minimize the effect of "blind velocities." Orig. art. has: 5 formulas and 4 figures.

SUB CODE: ~~02~~ 17, ~~13~~/ SUBM DATE: none

Card 2/2

ZAKHARKIN, D.F., ~~zh.~~zh.-mayor

Moving target selection apparatus in radar stations; material  
from foreign literature. Vest.protivozvzd.obor. no.2:24-26 F  
'61. (MIRA 14:2)

(Radar)

YEREMINA, Madeshda Vasil'yevna, nauchnyy sotrudnik; ZAKHARKIN, F.G.,  
red.; KAYDALOVA, M.D., tekhn.red.

[Golden corn] Eukuruza solotais. Khabarovsk, Khabarovskoe  
knizhnoe izd-vo, 1959. 27 p. (MIRA 14:12)

1. Birobidzhanskaya sel'skokhozyaystvennaya opyt'naya stantsiya  
(for Yermina).  
(Corn (Maize))



1. ZAKHARKIN, I.
2. USSR (600)
4. Concrete Construction
7. Mechanized preparation of concrete, Eng. Mast.ugl. 2 no. 3, 1953.

9. Monthly List of Russian Accessions, Library of Congress, APRIL 1953, Uncl.

ZAKHARKIN, L., I.,

Dec 50

USSR/Chemistry - Pharmaceuticals  
Medicine - Amoebic Dysentery

"New Synthesis of the Alkaloid Emetine," R. P. Yevstigneyeva, R. S. Livshits, L. I. Zakharkin, M. S. Baynova, N. A. Preobrazhenskiy

"Dok Ak Nauk SSR" Vol. LXXV, no 4, pp 539-542

In addn to being specific remedy against amoebic dysentery, emetine is effective against Trematodes and some bacteria which produce serious diseases in man and animals. Most probable formula for emetine, advanced by authors, corresponds to R. Robinson's formula based on theory of physiological conditions ("Nature," Vol CLXII, No 524, 155, 1943.) Formula has now been confirmed by authors, who carried out complete synthesis of racemic emetine in several different ways. Two reaction schemes illustrate authors' complete synthesis.

Pa. 173T23

ZAKHARKIN, L. I.

"Synthetic Investigations in the Field of the Alkaloid Emetine." Thesis for degree of Cand. Chemical Sci. Sub 3 Apr 50, Moscow Inst of Fine Chemical Technology imeni (M.V.) Lomonosov

Summary 71, 4 Sep 52, Dissertations Presented for Degrees in Science and Engineering in Moscow in 1950. From Vechernyaya Moskva, Jan-Dec 1950

ZAKHARKIN, L. I.

Chem Abs V48

1-25-54

Organic Chemistry

✓ Bromotrichloromethane. L. I. Zakharkin. *Atad. Nauk*  
 S.S.S.R. Inst. Org. Khim., Sintezy Org. Soedinenii, Sbornik 2, 14-19 (1952); cf. Kharasch, et al., *C.A.* 43, 3315a.—  
 Passage of a mixt. of 600 g. Br and 700 g.  $\text{CHCl}_3$  through a  
 tube packed with broken glass and heated to 420-50° with a  
 recycling of the material b. under 7b° until all Br is utilized  
 (2-3 passes) gave after washing with 10%  $\text{Na}_2\text{CO}_3$ , 80-85%  
 $\text{CBrCl}_3$ , b. 103-4°,  $n_D^{20}$  1.5032,  $d_4^{20}$  1.8942. G. M. K.

Chem  
 (2)

6/8/54  
 BW

SAKURAKIN, L. I.

Chemical Abst.  
Vol. 70 No. 5  
May 10, 1964  
Organic Chemistry

(6)  
Isoquinoline compounds. V. Synthesis of the natural  
alkaloid, emetine. R. P. Evstigneyev, R. S. Livshits,  
S. S. Bilnova, L. I. Sakurakin, and N. A. Prokhorovskii  
(Moscow Inst. Phys. Chem. Technol.). *J. Gen. Chem.*  
*U.S.S.R.* 22, 1611-1616 (1962) (Engl. translation). See *CA*  
47, 5919c. H. I. H.

74  
7-27-54

ZAKHARKIN, L.I.; PREOBRAZHENSKIY, N.A.

Isoquinoline compound series. VI. Synthesis of  $\beta$ -[1-(bromomethyl)propyl] glutaric acid and  $\beta$ -[1-hydroxymethyl)propyl]glutaric acid lactone. Zhur. Obshchey Khim. 22, 1890-5 '52. (MLRA 5:11)  
(CA 47 no.15:7507 '53)

1. M.V. Lomonosov Fine Chem. Tech.Inst., Moscow.

**"APPROVED FOR RELEASE: 03/15/2001**

**CIA-RDP86-00513R001963520001-4**

**APPROVED FOR RELEASE: 03/15/2001**

**CIA-RDP86-00513R001963520001-4"**

ZAKHARKIN, L. I.

"Isoquinoline compounds. Part 8. Condensation of  $\alpha'$ -substituted  $\beta$ -propylglutaric acids with homoveratrylamine". Zakharkin, L. I. and Preobrazhenskii, N. A. (p. 153)

SO: Journal of General Chemistry (Zhurnal Obshchei Khimii). 1953, Volume 23, No. 1.



"APPROVED FOR RELEASE: 03/15/2001

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**CIA-RDP86-00513R001963520001-4"**

USSR / Chemistry      Organic chemistry

Authors : Nersisyan, A. N., Zakharkin, L. I., Knet, V. N., and Freymann, R. M.

ABSTRACT : ACETAL, 2, 2, 2, 2-TETRAFLUOROETHYLENE, AND 1, 1, 1, 1-TETRAFLUOROETHYLENE

Submitted : August 23, 1953

USSR /

Dechlorination of tetrachloroalkoxycyclohexanes

Periodical : Dokl. AN SSSR, 97, Ed. 1, 91 - 94, July 1954

Abstract : The reaction leading to the conversion of tetrachloroalkoxycyclohexanes

Institution : Acad. of Sc. USSR, Institute of Elementary-Organic Compounds

Submitted : May 12, 1954

USSR/Chemistry - Allyl regrouping

Card 1/1 Pub. 22 - 30/56

Authors : Nemayanov, A. M., Academician; Froydina, R. KH.; and Zakharkin, L. I.

Title : Regrouping of allyl groups in 3,3-dichloropropene-1 in  $\beta$ -allyl  $\alpha$ -acyl acids

Periodical : Dok. AN SSSR 99/5, 781-783, Dec 11, 1954

Abstract : Another example of allyl regrouping in a dichloropropene system is presented. The conversion of 3,3-dichloro- $\alpha$ -alkoxy- $\beta$ -allyl-3-arylpentenals to  $\beta$ -allyl- $\alpha$ -alkoxy- $\gamma$ -arylpentenals is observed in an acetic acid solution of the

Institution : Academy of Sciences USSR, Institute of Elementary Organic Compounds

Submitted : OCTOBER 1, 1974

ZAKHARKIN, L. I.

USSR Chemistry - Synthesis

Card 1/2

Pub. 40 - 6/27

Authors : MEKESYANOV, A. N.; Zakharkin, L. I. and Freydina, R. Kh.

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 40-47, Jan-Feb 1955

... of  $\text{CCl}_3(\text{CH}_2)_n\text{COOH}$  and  $\text{CCl}_2$

Indexed

Submitted : March 31, 1954



Card 2/2

Pub. no - 6/27

Periodical : Izv. AN SSSR. Otd. khim. nauk 1, 40-47, Jan-Feb 1955

Abstract : It is shown that  $\gamma$ ,  $\gamma$ -dichlorovinylacetic acid has a higher dissociation constant than  $\gamma$ ,  $\gamma$ -trichlorobutyric acid. The effects of the  $\text{CCl}_2$  and  $\text{CF}_2$  groups in higher  $\alpha$ ,  $\omega$ ,  $\omega$ -trihaloacetic acids on the dissociation constants are described. Eleven references: 5 USA, 4 USSR and 2 German (1901-1954).

Authors : Semakova, A. N., and Semakova, L. I.

Title : *Reaction of omega-chlorocarboxylic acids and some of their conversion*

Periodical : Izv. AN SSSR. Otd. khim. nauk 2, 224 - 232, Mar-Apr 1955

Abstract : The reactivity of numerous omega-chlorocarboxylic acids was investigated. The products obtained from the hydrolysis of tetrachloro alkanes, which were formed during the reaction of ethylene with carbon tetrachloride, are described. A thorough study of reaction of omega-chlorocarboxylic acids showed that these acids could successfully substitute for the homologous bromo acids. Fifteen references: 7 USA, 1 USSR, 3 French, 3 German and 1 Dutch (1894-1954).

Institution : Acad. of Sc., USSR, Inst. of Organoelemental Compounds

Submitted : April 20, 1954

Zakharin, L.I.

6

Action of organomagnesium compounds on acetals of chloropropionaldehydes. Synthesis of acetals of  $\alpha,\beta$ -acetyl-  
enic aldehydes. L. I. Zakharin (Inst. Nitrogen Compds. of Acad. Sci., Moscow, U.S.S.R.) Dokl. Akad. Nauk S.S.S.R. 105, 985-6 (1953).

Chem. To EtONa (from 21 g. Na and 250 ml. EtOH) was added 160 g. 1,1,3-trichloro-3-ethoxy-1-propene and after 10 min. 0.5 g. powd. KOH added and the mixt. heated 1.5 hrs. After eq. treatment and extr. with Et<sub>2</sub>O there was obtained 82%  $\text{ClC}(\text{OEt})\text{CH}(\text{OEt})$ , b. 55-6°, n<sub>D</sub> 1.4307, d<sub>4</sub> 1.0300 and 35 g.  $\text{ClCH}_2\text{CHClCH}(\text{OEt})$ . The former gave 2,4-dinitrobenzylhydrazine, m. 127-7.5°. Prep'd. similarly was 58%  $\text{ClC}(\text{OEt})\text{CH}(\text{OEt})$ , b. 109.5-10.5°, 1.4410, 0.9820. These were treated with RMgX yielding the corresponding  $\text{RC}(\text{OEt})\text{CH}(\text{OEt})$  in 40-70% yields (R, n, b.p., n<sub>D</sub>, d<sub>4</sub> given resp.): Pr, Et, b. 79-80°, 1.4333, 0.8108; iso-Pr, Et, b. 73-5°, 1.4321, 0.8002; Bu, Et, b. 69-100°, 1.4328, 0.8771; iso-Bu, Et, b. 91-2°, 1.4307, 0.8168; C<sub>10</sub>H<sub>7</sub>, Et, b. 123-4°, 1.4395, 0.8760; C<sub>10</sub>H<sub>7</sub>, Bu, b. 150-5°, 1.4453, 0.8553; C<sub>10</sub>H<sub>7</sub>, Et, b. 158-60°, 1.4419, 0.8068; Ph, Et, b. 116-7°, 1.5211, 0.8950; Ph, Bu, b. 123-9°, 1.5255, 0.8510; C<sub>10</sub>H<sub>7</sub>, Bu, b. 178-9°, 1.5510, 1.0128. Heating 21 g.  $\text{ClC}(\text{OEt})\text{CH}(\text{OEt})$  with 5 g. powd. Na in Et<sub>2</sub>O followed by treatment with 17 g. Me<sub>2</sub>SO, gave 75% tetraoldehyde di-Et acetal, b. 99.5-11°, 1.4359, 0.9820. The reaction mixt. from 5 g. Na and 16.2 g.  $\text{ClC}(\text{OEt})\text{CH}(\text{OEt})$  in Et<sub>2</sub>O was treated with 10.5 g. cyclohexanone after 0.5 hr. heating and quenching in H<sub>2</sub>O there was obtained 80% 1,2-diol, b. 116-7°, 1.4359, 0.9820.

ZAKHARKIN, L. I.

USSR/Organic Chemistry - Synthetic Organic Chemistry, E-2

Abst Journal: Referat Zhur - Khimiya, No 1, 1957, 800

Author: Nesmeyanov, A. N., Freydlina, R. Kh., and Zakharkin, L. I.

Institution: None

Title: The Investigation of the Reactions of Polychlorohydrocarbons and Related Compounds

Original  
Periodical: Uspekhi khimii, 1956, Vol 25, No 6, 665-704

Abstract: A detailed survey with a bibliography of 93 titles.

Card 1/1

Zakharkin, L. I.

USSR/Organic Chemistry - Theoretical and General Questions  
on Organic Chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4228

Author : Nesmeyanov, A.N., Freydlina, R.Kh., Zakharkin, L.I.,  
Belyavskiy, A.B.

Title : Action of Nucleophilic Substances on Compounds of the  
Structure  $CCl - CH = CRR'$ .

Orig Pub : Zh. obshchey khimii, 1956, 26, No 4, 1070-1082

Abstract : By dehydrobromination of 1,1,1-trichloro-3-bromobutane  
(I), 1,1,1-trichloro-3-bromo-3-phenylpropane (II), 1,1,  
1-trichloro-3-bromo-3-methylbutane (III) and 1,1,1-tri-  
chloro-3-bromo-4, 4-dimethylbutane (IV) (synthesized by  
addition of  $CBrCl_3$  to the corresponding olefins) were  
prepared, respectively: 1,1,1-trichlorobutene-2 (V),  
1,1,1-trichloro-3-phenylpropene-2 (VI), 1,1,1-trichloro-  
3-methylbutene-2 (VII) and 1,1,1-trichloro-4,4-dimethyl-  
pentene-2 (VIII). Structure of VI was confirmed by

Card 1/14

-3 -

USSR/Organic Chemistry - Theoretical and General Questions  
on Organic Chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4228

which is attributed to spatial hindrances. In an alcoholic medium  $(C_2H_5)_2NH$  reacts with V and VI to form mixtures of alkoxy- and amino- derivatives, while with VII and VIII only alkoxy-derivatives are formed. With  $(C_2H_5)_2NH$  alone, without alcohol, V and VI form amino-derivatives, while VII does not react even at  $110^\circ$ . On action of  $NH_3$  and piperidine (XI), in an alcoholic medium, VII forms a small amount of amino-derivatives. The same course of the reaction has been ascertained on interaction of V, VI and VII with  $Na_2S$  in alcoholic medium: V and VI form mixtures of O- and S-derivatives, while VII yields only O-derivatives. The authors draw the conclusion that the reactivity of the investigated compounds depends to a large extent upon the nature of the substituents at the center of action of the NP. With decrease of the electrophilic nature (EP) of the compound under

Card 3/14

- 5 -

USSR/Organic Chemistry - Theoretical and General Questions  
on Organic Chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4228

study ( $V > VI > VIII > VII$ ) the rate of alkylation at the O-atom increases and that at the N- or the S-atom decreases. From previous work, (see above-cited reference), it follows that EP of 1,1,1-trichloropropene is greater than that of V. An analogy is traced between the reactions under study and the alkylation of metal derivatives of tautomeric systems, taking place with transfer of the reaction center. In the former case, there is alkylated a mixture of two substances comprising different centers of EP attack, and in the latter case both these centers are bound into a  $\sigma$  system of  $\pi$ -conjugation (keto-enolic, lactim-lactamic). It is shown that V, VI and VII react with  $C_6H_6$  in the presence of  $AlCl_3$ , to form, respectively, 1,1-dichloro-3-phenylbutene-1 (XII), 1,1-dichloro-3,3-diphenylpropene-1 (XIII) and 1,1-dichloro-3-methyl-3-phenylbutene-1 (XIV). It was found that

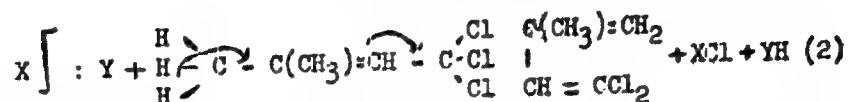
Card 4/14

- 6 -

USSR/Organic Chemistry - Theoretical and General Questions  
on Organic Chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4228



the NP-reagent on  $\sigma$ ,  $\pi$ ,  $\sigma$ -conjugated system (see scheme 2). High yield of XV from X and its low yield from VII are indicative of the fact that VII reacts with NP-reagents in accordance with scheme (1) without any isomerization. Noted is the similarity in behavior of the  $Cl_3C$ -group of VI and of  $C_6H_5CCl_3$  (hydrolysis by 90%  $CH_3COOH$ , disproportionation with formation of  $ClCH_2COCl$  on heating with  $ClCH_2COOH$ ). There is proposed a new scheme (cf., Kharasch, J. Amer. Chem. Soc., 1947, 69, 1100, 1105), of alkaline hydrolysis of the products of addition of  $CCl_3$  to olefins:

Card 6/14

- 8 -



USSR/Organic Chemistry - Theoretical and General Questions  
on Organic Chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4228

64%, BP 91-92°/1 mm,  $n_D^{20}$  1.5710,  $d_4^{20}$  1.3217. On dehydrobromination with alkali in  $C_2H_5OH$  VI reacts with alcohol. 153 g III in 50 ml alcohol treated with 45 g KOH in 180 g alcohol (0°) to get XV, yield 3.5 g, BP 30-31°/8 mm,  $n_D^{20}$  1.5027, and VII, yield 60.5%, BP 45-46°/8 mm,  $n_D^{20}$  1.4822,  $d_4^{20}$  1.2497. From 63 g XVI and 47 g KOH in 150 ml  $CH_3CH$  (15-20°, 1 day) are obtained XV, yield 5.1 g, and XVII, yield 71%, BP 51-52°/10 mm,  $n_D^{20}$  1.4628,  $d_4^{20}$  1.1418. In the same manner from 50 g XVI, 35 g KOH and 100 ml  $C_2H_5OH$  are obtained 12 g XV and XVIII, yield 14 g, BP 72-73°/24 mm,  $n_D^{20}$  1.4616,  $d_4^{20}$  1.1101. 17 g XVII and  $C_2H_5ONa$  (from 6 g Na) in 80 ml absolute alcohol boiled 10 hours, added 8 g KOH in 10 ml water and boiled 6 hours, to get  $(CH_3)_2C=CHCOOH$ , yield 4.2 g, MP 69-70° (from water). Into 39.5 g XVII HCl (gas) is passed for 2.5 hours, stratified liquid is poured into HCl, bottom layer is separated,

Card 8/14

- 10 -

USSR/Organic Chemistry - Theoretical and General Questions  
on Organic Chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4228

and therefrom is obtained X, yield 30.1 g, BP 58-58.5°/15 mm,  $n_{D}^{20}$  1.4847,  $d_4^{20}$  1.2527. X is also obtained by passing HCl (gas) (-5° to -7°, 3 hours) into 14 g XV in presence of 1 g ZnCl<sub>2</sub>, yield 52%, BP 64°/25 mm. From 25 g 4,4-dimethylbutene-1, 60 g CBrCl<sub>3</sub> and 1 g of diisotride of azo-bis-isobutyric acid (autoclave, 100-105°, 6 hours) is obtained IV, yield 38 g, BP 90°/5 mm,  $n_{D}^{20}$  1.5030,  $d_4^{20}$  1.4792. From 0.11 mole IV and 0.33 mole (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH (~ 100°, 18 hours) is synthesized VIII, yield 70%, BP 64-65°/10 mm,  $n_{D}^{20}$  1.4725,  $d_4^{20}$  1.1403. Ozonation of VIII yields the chloral. From 35.6 g V and CH<sub>3</sub>ONa (from 4.98 g Na in 50 ml CH<sub>3</sub>CH) is obtained (~ 100°, 2.5 hours) 1,1-dichloro-3-methoxybutene-1 (XX), yield 50%, BP 64°/57 mm,  $n_{D}^{20}$  1.4580,  $d_4^{20}$  1.1722. 15.9 g V and 18.3 g (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH (boiled 8 hours) form 1,1-dichloro-3-diethylamino-butene-1 (XXI), yield 50%,

Card 9/14

- 11 -

USSR/Organic Chemistry - Theoretical and General Questions  
on Organic Chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4228

BP 79.5-80°/14 mm,  $n_D^{20}$  1.4690,  $d_4^{20}$  1.0470; hydrochloride, MP 167.5°. Same amounts of V and  $(C_2H_5)_3NH$  heated in 40 ml  $CH_3OH$ , which gives 30% XXI and XX,  $n_D^{20}$  BP 40-41°/15 mm. From 32 g V, 32.8 g  $CH_3COONa$  and 0.5 g KI, in 50 g  $CH_3COOH$  ( $\sim 100^\circ$ , 18 hours) is obtained 1,1-dichloro-3-acetoxybutene-1 (XXII), yield 59%, BP 83-84°/26 mm,  $n_D^{20}$  1.4590,  $d_4^{20}$  1.2234. Structure of XXII is established by converting it by the action of alcohol into XIX, BP 63°/6 mm (in the paper: 1,1-dichloro-3-hydroxybutene-2). Heating of 30 g V and 29 g  $Na_2S \cdot 9H_2O$  in 80 ml alcohol and 10 ml water ( $\sim 100^\circ$ , 6 hours) gives bis-(1,1-dichloro-3-methylpropene-1-yl)-sulfide, yield 40%, BP 104°/5 mm,  $n_D^{20}$  1.5345,  $d_4^{20}$  1.3156, and 1,1-dichloro-3-ethoxybutene-1. From 24.4 g V and sodium malonic ester (from 4.6 g Na and 32 g malonic ester in 80 ml absolute alcohol) is obtained (boiling 3 hours) the ethyl ester of 5,5-dichloro-

Card 10/14

- 12 -

USSR/Organic Chemistry - Theoretical and General Questions  
on Organic Chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4228

-3-methyl-2-carbethoxypentene-4-ic acid (XXIII), yield 70%, BP 107°/1 mm,  $n_{D}^{20}$  1.4605,  $d_4^{20}$  1.1829. 20.7 g XXIII are hydrolyzed (by boiling with HCl and  $CH_3COCH_3$ ) and decarboxylated to 5,5-dichloro-3-methylpentene-4-ic acid, yield 85.7%, BP 102°/1 mm,  $n_{D}^{20}$  1.4800,  $d_4^{20}$  1.2739. By interaction of 10 g V, 1.2 g  $AlCl_3$  and 25 ml  $C_6H_6$  (stirred 30 minutes) is obtained XII, yield 70%, BP 73-74°/1.5 mm,  $n_{D}^{20}$  1.5423,  $d_4^{20}$  1.1702. On action of  $Cl_2$  XII forms 1,1,1,2-tetrachloro-3-phenylbutane, BP 107-108°/1.5 mm,  $n_{D}^{20}$  1.5568,  $d_4^{20}$  1.3634. From 36 g IX and 36.5 g  $(C_2H_5)_2NH$  ( $\sim 100^\circ$ , 16 hours) are obtained XXI, yield 13.8 g, BP 84-87°/21 mm, and 20.6 g IX. Interaction of 15 g VI and 5.5 g KOH in 25 ml absolute  $C_2H_5OH$  (15-20°, 16 hours) gives 1,1-dichloro-3-ethoxy-3-phenylpropene-1 (XXIV), yield 87%, BP 90-91°/1 mm,  $n_{D}^{20}$  1.5308,  $d_4^{20}$  1.1822. From 11 g VI and 12 g

Card 11/14

- 13 -

USSR/Organic Chemistry - Theoretical and General Questions  
on Organic Chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4228

$(C_2H_5)_2NH$  in 25 ml absolut  $C_2H_5CH$  (heating 8 hours)  
are obtained XXIV, yield 4.5 g, and  
1,1-dichloro-3-diethylamino-3-phenylpropene-1, yield  
4.8 g, BP 98-99°/1 mm,  $n_D^{20}$  1.5335,  $d_4^{20}$  1.1116; hydro-  
chloride MP 149-150° (from alcohol-petroleum ether).  
From 11 g VI, 3 g  $AlCl_3$  and 20 ml  $C_6H_6$  is synthesized  
XIII, yield 76%, BP 142-143°/1 mm,  $n_D^{20}$  1.5951,  $d_4^{20}$   
1.2180. By interaction of 17 g VII and 8.5 g KOH in 40  
ml  $CH_3OH$  (15-20°, 16 hours) are obtained a small amount  
of XV and XVII, yield 82%, BP 47-48°/7 mm. Interaction  
of 10 g VII and 16 g  $(C_2H_5)_2NH$  in 30 ml  $CH_3OH$  (heated  
10 hours) gives XV and XVII, yield 77%. BP  
57-58°/14 mm. From 10 g VII and 5 g  $NH_3$  in 40 ml absolu-  
te alcohol (in ampoule, 90-95°, 4 hours) is obtained  
XVIII, with a yield of 6 g, and 1,1-dichloro-3-amino-3-  
methylbutene-1, yield 0.9 g, BP 64-65°/12 mm,  $n_D^{20}$

- 14 -

Card 12/14

USSR/Organic Chemistry .. Theoretical and General Questions  
on Organic Chemistry

E-1

Abs Jour : Referat Zhur - Khimiya, No 2, 1957, 4228

petroleum ether). From 10 g VII and 40 ml  $C_2H_5OH$  (15-20°, for several days) is obtained XVIII. Interaction of 10 g VIII and  $CH_3ONa$  (from 1.15 g Na in 50 ml  $CH_3CH_2OH$ ) gives (on boiling for 30 hours) 1,1-dichloro-3-methoxy-4,4-dimethylpentene-1 (XXV), yield 50%, BP 60-61°/9 mm,  $n_D^{20}$  1.4620,  $d_4^{20}$  1.0755. From 7 g VIII and 5 g  $(C_2H_5)_2NE$  in 15 g  $CH_3OH$  ( $\sim 100^\circ$ , 19 hours) is obtained XXV, yield 2.2 g.

Card 14/14

- 16 -

2. A. HARKIN, L. I.  
MESKHYANOV, A.M., akademik; ZAKHARKIN, L.I.; FRYDLINA, R.Kh.

The condensation of  $\gamma,\delta$ -trichlorocrotonic acid,  $\gamma,\delta$ -dichlorocrotonic acid and  $\gamma$ -bromocrotonic acid with benzene in the presence of aluminum chloride. Dokl. AN SSSR 111 no.1:114-116 M-D '56. (MLRA 10:2)

1. Institut elementoorganicheskikh soedineniy Akademii nauk SSSR.  
(Crotonic acid, (Benzene))

**"APPROVED FOR RELEASE: 03/15/2001**

**CIA-RDP86-00513R001963520001-4**

**APPROVED FOR RELEASE: 03/15/2001**

**CIA-RDP86-00513R001963520001-4"**



ZAKHARKIN, L.I., FREYDLINA, R., NESMEYANOV, A.N., FREYDLINA, R.Ich., KOST, V.N.

AS USSR

"Homolytic Isomerisation in Polyhalogenalkenes," paper submitted  
at 16th International Congress of Pure and Applied Chemistry, Paris,  
18-24 July 1957

ZAKHARKIN, L. I., FREYDLINA, R. S., IERMEYANOV, A. N., VASILYEVA, E. Y., PETROVA, N. G.,  
and KARAPETIAN, S. A.

"Polymerization of ethylene with telomers and a new synthesis of amino acids," a paper presented at the 9th Congress on the Chemistry and Physics of High Polymers, 28 Jan-2 Feb 57, Moscow, Organic Chemistry Research Inst.

B-3,084,395

ZAKHARKIN, L.I.

62-11-7/29

AUTHORS:

Zakharkin, L.I., Korneva, V.V.

TITLE:

Allylic Rearrangements of 1.1-Dichloro-3-Phenylpropene-1 and Related Compounds (Allil'nyye peregruppirovki i blizkikh soedineniy). 1.1-dikhlor-3-fenilpropena-1 i blizkikh soedineniy).

PERIODICAL:

Izvestiya AN SSSR, Otdelenie Khimicheskikh Nauk, 1957, Nr 11, pp. 1344-1348 (USSR)

ABSTRACT:

Here it is demonstrated that under the influence of the sodium-alcoholate on 1.1-dichloro-3-phenylpropene-1 an allyl-prototropic rearrangement to 1.1-dichloro-3-phenylpropene-2 takes place. In a further reaction with the sodium-alcoholate diethylacetal of the cinnamaldehyde and the diethylketal of the phenylethynylketone develop. It is demonstrated that under the influence of the sodium-alcoholate on 1.1-dichloro-3-acetoxy-3-phenylpropene-1 the diethylketal of the phenylethynylketone is obtained. There are 12 references, 5 of which are Slavic.

ASSOCIATION:

Institute for Elementorganic Compounds of the AN USSR. (Institut elementoorganicheskikh soedineniy Akademii nauk SSSR)

ZAKHARKIN, L. I.

AUTHORS: Zakharkin, L. I., and Okhlobystin, O. Yu. 20-2-20/50

TITLE: The Utilization of Aluminum Trialkyls in the Synthesis of Elemental Organic Compounds (Ispol'zovaniye alyuminiytrialkilov dlya sinteza elementoorganicheskikh soyedineniy).

PERIODICAL: Doklady AN SSSR, 1957, Vol. 116, Nr 2, pp. 236-238 (USSR)

ABSTRACT: In connection with the fact that organoaluminum compounds were easily accessible in recent times the problem naturally rises of their utilization in the synthesis of other element-organic compounds. In patent publications production-methods were described of organozinc, organocadmium and organomercury compounds of the type  $RMeX$ , as well as of trialkylboranes from haloid compounds of the same elements and from a mixture of alkylaluminum-halides which forms on the action of appropriate haloidalkyls on aluminum:

$3 RX + 2 Al \rightarrow RAlX_2 + R_2AlX$ . As far as this reaction only takes place with the lower alkyls (R not higher than  $C_3H_7$ ), this method can not be considered general enough. In the present paper the authors studied the interaction of

Card 1/4

The Utilization of Aluminum Trialkyls in the Synthesis of  
Element Organic Compounds

20-2-20/50

beron-, antimony-, arsenic-, phosphorus-, tin- and mercury-halides with triethylaluminum and tri-isobutylaluminum. In all cases investigated an exchange reaction takes place under formation of an aluminum halide and of alkyl derivatives of the elements taken. On addition of trifluoroboro-ethydrate to tri-isobutyl-aluminum, triisobutylboron forms at 60-65°C. The same forms on blowing gaseous trifluoroboron through a triethylaluminum solution in decahydronaphthalene. The interaction of tri-isobutyl-aluminum-ethydrate with a suspension of trifluor-antimony in ether takes place just as easily. The interaction of tri-isobutyl-aluminum with arsenic trichloride in ether does not lead to trialkylarsine; chief products are, however: isobutyl-trichloroarsine and di-isobutyl-chloroarsine. The interaction of tri-isobutyl-aluminum with phosphorus trichloride is more complicated. The formation of a complex of the reaction products with chloroaluminum takes place as the result of an energetic reaction (independently of the type of solvent). From the reaction mass

Card 2/4

The Utilization of Aluminum Trialkyls in the Synthesis of Elemental Organic Compounds 20-2-20/50

isobutyldichlorophosphine can be distilled off in a vacuum. On further heating of the rest a radical decomposition takes place under formation of volatile products and elementary phosphorus. The interaction of equimolecular amounts of tri-isobutyl or tri-ethyl-aluminum with mercuric bromide or sublimate in ether or in hexane chiefly leads to symmetric dialkyl derivatives of mercury: a) Diiso-butyl-mercury and b) bromo-isobutyl-mercury. Diethyl-mercury was obtained from sublimate and triethylaluminum in hexane. Stannic tetrachloride yields tetra-isobutyl-tin on the action of tri-isobutyl-aluminum in heptane at 40-48°C (after decomposition by a NaOH-solution). Besides, tri-isobutyl-tin-oxide can be isolated by distillation of the rest over sodium, apparently by dehydration of the corresponding hydroxide. Thus (iso-C<sub>4</sub>H<sub>9</sub>)<sub>3</sub>SnCl forms in the case of interaction of tri-isobutyl-aluminum and stannic tetrachloride. There are 14 references, 1 of which is Slavic.

Card 3/4

The Utilization of Aluminum Trialkyls in the Synthesis of Elemental Organic Compounds 20-2-20/50

ASSOCIATION: Institute for Element Organic Compounds AN USSR  
(Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)

PRESENTED: By A. N. Nesmeyanov, Academician, May 8, 1957

SUBMITTED: May 7, 1957

AVAILABLE: Library of Congress

Card 4/4

Production of Aldehydes by Reduction of Nitriles With  
Diisobutylaluminum Hydride.

20-3-20/16

attain 80 to 90% of the theoretically possible. The reaction concerned can be performed in various solvents (ether, benzol, heptane, a. o.), or without such solvents, what involves many advantages. According to the nature of the nitrile, temperatures from 0 to 40° were chosen. In the case of almost equimolar ratios of both participants in the reaction, nitriles were never reduced up to the amines. The decomposition of the transition product of the diisobutylaluminum hydride to the nitrile should be carried out with great precaution, especially in the case of such readily changeable aldehydes as phenylacetic acid aldehyde. The transition product of the  $(i-C_4H_9)_2 AlH$  to capronityl cannot be distilled in 1 mm vacuum without decomposition. Reduced yields of phenylacetic aldehyde and of 1,1 dichlorhexen-1-Al-6 can be explained by the partial compaction ("uplotneniye") of these aldehydes, This can be remedied by the addition of 2,4 - dinitrophenylhydrazine, so that the yield of corresponding 2,4 - dinitrophenylhydrazon comes to 80 and 72%. The above report is followed by an experimental part with the conventional data. There are 1 table, and 8 references, none of which are Slavic.

Card 2/3

APPROVED FOR RELEASE: 03/15/2001

CIA-RDP86-00513R001963520001-4"

Production of Aldehydes by Reduction of Nitriles With  
Diisobutylaluminum Hydride.

20-3-20/16

ASSOCIATION: Institute of Elemental-Organic Compounds AN USSR (Institut elemento-organicheskikh soedineniy Akademii nauk SSSR).

PRESENTED: May 8, 1957, by A. N. Nesmeyanov, Academician.

SUBMITTED: May 7, 1957.

AVAILABLE: Library of Congress.

Card 3/3



**ZAKHARKIN, L. I.**

**AUTHORS:**

Zakharkin, L. I., Gavrilenko, V. V., Okhlobystin, O. Yu. 62-1-18/29

**TITLE:**

The Action of Triethyl Aluminum and Diisobutyl Aluminum Hydride on Metal Chlorides of Group VI in the Presence of Carbon Monoxide  
 Synthesis of the Chromides, Molybdenum, and Tungsten Carbonyls  
 (Deystviye trietil'aluminiya i diizobutil'aluminiygidrida na khloridy metallov VI grupy v prisutstvii okisi ugl'roda. Sintez karbonilov khroma, molibdena i vol'frama)

**PERIODICAL:**

Izvestiya AN SSSR, Otdeleniye Khimicheskikh Nauk, 1958  
 Nr 1, pp 100 - 102 (USSR)

**ABSTRACT:**

The action of triethylaluminum and diisobutylaluminumhydride on the above mentioned chlorides was for the first time investigated by Jab and Cassal (reference 1). Both found, that carbonyles of chromium, molybdenum, and tungsten are formed in the reaction. Later this method was investigated by means of magnesium-organic compounds, i.e. indifferent variants. The authors show in this paper that for the obtaining of  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$  and  $\text{Cr}(\text{CO})_6$  triethylaluminum and diisobutylaluminumchloride can be used with success, i.e. in carrying out the reaction of the chlorides of the metals of the 6th group with triethylaluminum in etheric solution. In the reaction under the same conditions with diisobutylaluminumhydride  $\text{Cr}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  were obtained (with a

Card 1/2

The Action of Triethyl Aluminum and Diisobutyl Aluminum Hydride on (0-1-10/29)  
Metal Chlorides of Group VI in the Presence of Carbon Monoxide. Synthesis  
of the Chromium-, Molybdenum-, and Tungsten Carbonyls

yield of 73 - 75%.) The synthesis of the triethylaluminum and triisobutylaluminum (of which diisobutylaluminumhydride was produced) was carried out by the authors corresponding to the reaction of Ziegler, Cellert, Zosel (reference 5) from aluminum, hydrogen, and the corresponding olefin. There are 5 references.

ASSOCIATION: Institute of Elemental-Organic Compounds, AS USSR (Institut elementoorganicheskikh soedineniy Akademii nauk SSSR).

SUBMITTED: July 12, 1957

AVAILABLE: Library of Congress

1. Triethylaluminum-Synthesis
2. Triisobutylaluminum-Synthesis
3. Chromium carbonyl-Synthesis
4. Molybdenum carbonyl-Synthesis
5. Tungsten carbonyl-Synthesis
6. Diisobutylaluminumhydride-Production
7. Metal chlorides-Chemical reactions
8. Triethylaluminum-Chemical reactions
9. Diisobutylaluminumhydride-Chemical reactions
10. Carbon monoxide-Applications

Card 2/2

SOV/62-58-10-21/25

AUTHORS: Zakharkin, L. I., Okhlobystin, O. Yu.

TITLE: Regrouping of Aluminum Trialkyls (Perogrupperovka alyuminiy-trialkilov)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1958, Nr 10, pp 1278 - 1278 (USSR)

ABSTRACT: The authors found by the example of triisopropyl aluminum and tri-sec.-butyl aluminum that secondary aluminum trialkyls regroup into primary aluminum trialkyls on heating. The described method of the production of triisopropyl aluminum from  $(i-C_3H_7)_2Hg$  and Al does not only yield triisopropyl aluminum, as the authors suggested (Ref 1), but also the mixture of triisopropyl aluminum and tripropyl aluminum which can be separated by fractionation. The triisopropyl aluminum produced in this way can be completely converted to tripropyl aluminum in a sealed ampoule. Tri-sec.-butyl aluminum produced in the reaction  $(sec. C_4H_9)_2Hg$  with aluminum can be converted under the same conditions by regrouping into

Card 1/2

SOV/52-58-10-21/25

Regrouping of Aluminum Trialkyls

tri-n.butyl aluminum. In this case  $\beta$ -butylene and di-n.  
butyl aluminum hydride could partly form. Tri-n. butyl  
aluminum could be identified by means of n.butyl  
mercury bromide; boiling point  $136^{\circ}$ . There is 1 reference.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR  
(Institute of Elementary Organic Compounds AS USSR)

SUBMITTED: June 6, 1958

Card 2/2

SOV/62-58-12-7/22

5(3)  
AUTHORS:

Zakharkin, L. I., Sorokina, L. P.

TITLE:

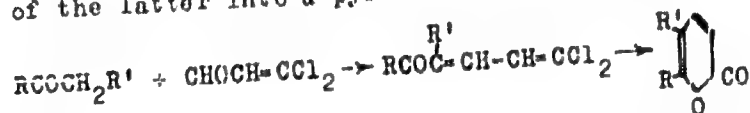
Condensation of  $\beta,\beta$ -Dichloro Acrolein With Carbonyl Compounds and the Conversion of Condensation Products Into  $\alpha$ -Pyrone Derivatives (Kondensatsiya  $\beta,\beta$ -dikhlorakroleina s karbonil'nymi soyedineniyami i prevrashcheniye produktov kondensatsii v proizvodnyye  $\alpha$ -pirona)

PERIODICAL:

Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 12, pp 1445-1451 (USSR)

ABSTRACT:

In the present paper the authors investigated the condensation of  $\beta,\beta$ -dichloro acrolein with some carbonyl compounds, which leads to the production of dichloro diene ketenes. Besides, they investigated the possibility of a closing of the cycle of the latter into  $\alpha$ -pyrone derivatives:



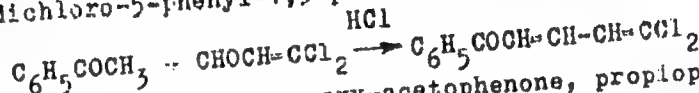
Card 1/3

With aliphatic aromatic ketones the reaction with  $\beta,\beta$ -dichloro

SOV/62-58-12-7/22

Condensation of  $\beta,\beta$ -Dichloro Acrolein With Carbonyl Compounds and the  
Conversion of Condensation Products Into  $\alpha$ -Pyrone Derivatives

acrolein in the presence of hydrogen chloride takes place easily. Thus, acetophenone with  $\beta,\beta$ -dichloro acrolein yields 1,1-dichloro-5-phenyl-1,3-pentadiene-5- $\alpha$ -on:

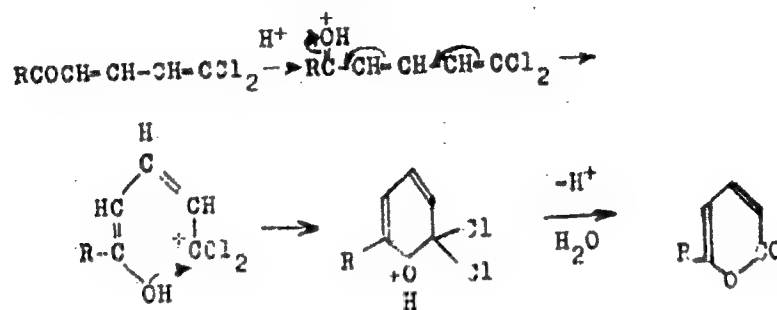


p-chloro-acetophenone, p-oxy-acetophenone, propiophenone and n-butyrophenone react in a similar way. With respect to the mechanism of the closure of the cycle of the dichloro pentadiene system into an  $\alpha$ -pyrone system the following considerations may be made: It may be assumed that in acid medium originally a hydrolysis takes place of the dichlorovinyl group into a carboxyl group with a subsequent closure of the cycle of the formed keto acids. In this case an addition of the proton to the  $\text{CCl}_2$ -CH-group takes place. The assumption, however, that the proton affiliates to the end of the conjugated system, i.e. to the carbonyl oxygen, seems more probable. The process of cyclization can then be represented as follows:

Card 2/3

SOV/62-58-12-7/22

Condensation of  $\beta,\beta$ -Dichloro Acrolein With Carbonyl Compounds and the  
Conversion of Condensation Products Into  $\alpha$ -Pyrone Derivatives



There are 4 references, 1 of which is Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR  
Institute of Elementorganic Compounds, Academy of Sciences,  
USSR)

SUBMITTED: April 5, 1957  
Card 3/3

ZAKHARKIN, L.I.; GAVRILENKO, V.V.

Action of carbon dioxide on aluminum trialkyls. Dokl. AN SSSR.  
118 no.4:713-715 F '58. (MIRA 11:4)

1. Institut elementoorganicheskikh soedineniy Akademii nauk SSSR.  
Predstavleno akademikom A.N. Nesmeyanovym.  
(Aluminum organic compounds)  
(Carbon dioxide)  
(Acids)



SOV/62-59-1-29/38

5(3)

AUTHORS:

Zakharkin, L. I., Gavrilenko, V. V.

TITLE:

Interaction of Halogens With Aluminum Trialkyls (Vzaimodeystviye galojodov s alyuminiytrialkilami)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye Khimicheskikh nauk, 1959, Nr 1, pp 166 - 168 (USSR)

ABSTRACT:

In the present communication the authors report on the investigation of the effect of chlorine, bromine, iodide on a number of aluminum trialkyls. Aluminum trialkyls react very strongly with halogens without solvent even at low temperatures (down to  $-78^{\circ}$ ). The effect of chlorine was investigated with triisobutyl aluminum, tri-n-butyl aluminum, tripropyl aluminum and tri-n-hexyl aluminum. Thus isobutyl chloride, 1-chloro butane, 1-chloro propane and 1-chloro hexane were obtained accordingly. The chlorination was carried out at  $-35$  and  $-200$ . The yield of alkyl chlorides amounted to 60-70%. Besides monochlorine derivatives also higher chlorine derivatives were obtained, especially at an excess of chlorine. In addition to that, the aluminum trialkyl mixture synthesized from triethyl aluminum and

Card 1/ 2

Interaction of Halogens With Aluminum Trialkyls

SDV/62-19-1-29/38

ethylene was chlorinated. 1-chloro butane, 1-chloro hexane and 1-chloro octane were separated therein. The reaction with bromine was investigated with triisobutyl aluminum, tri-n-butyl aluminum, tripropyl aluminum and tri-n-hexyl aluminum. At -20 and -25° only 2/3 of the theoretically required bromine quantity reacted. The yield of alkyl bromides amounted to 60-70%. By the action of bromine on the reaction product of trimethyl aluminum and isobutylene neopentyl bromide was precipitated in addition to methyl bromide. The effect of iodide was investigated with triethyl- and triisobutyl aluminum. The yield of alkyl iodides amounted to ~ 60%. Under given conditions isomerization of halide alkyls was not observed in one of the cases investigated. There are 5 references, 2 of which are Soviet.

ASSOCIATION:

Institut elementoorganicheskikh soedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED:

June 6, 1958

Card 2/2

5(3)

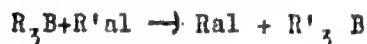
SOV/62-59-1-37/38

AUTHORS: Zakharkin, L. I., Okhlobystin, O. Yu.

TITLE: On the Reaction of Realkylation in the Aluminum and Boron Trialkyl Series (O reaktsii perealkilirovaniya v ryadu alyuminiy- i bortrialkilov)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 1, pp 181 - 181 (USSR)

ABSTRACT: The authors write in a letter to the editor: On heating trialkyl or triaryl boron  $R_3B$  with trialkyl aluminum  $R'_3Al$  a reaction of realkylation occurs. Thus  $R'_3B$ ,  $R_3Al$  and products of incomplete realkylation of initial trialkyl aluminum are formed:



$al = 1/3 Al$ ;  $R = n-C_4H_9$ ,  $i-C_4H_9$ ,  $C_6H_5$ ;  $R' = CH_3, C_2H_5$ .

Because of the high reaction temperature (120-180°) the olefin is separated from the  $R_3Al$  formed in some cases to a considerable degree. Consequently corresponding dialkyl

Card 1/3

On the Reaction of Realkylation in the Aluminum and Boron    SOV/62-59-1-37/38  
Trialkyl Series

aluminum hydrides are produced. In the interaction of triisobutyl boron with triethyl aluminum, for instance, triethyl boron and diisobutyl aluminum hydride were obtained. On gradual heating (up to  $180^{\circ}$ ) of the mixture of triphenyl boron with a double quantity of triethyl aluminum triethyl boron is slowly distilled in pure nitrogen current. After the distillation of the mixture  $(C_2H_5)_2AlC_6H_5$  and  $C_2H_5Al(C_6H_5)_2$  in vacuum triphenyl aluminum remains in the residue. Under equal conditions, trimethyl boron is synthesized from  $(C_6H_5)_3B$  and  $(CH_3)_3Al$  with a yield of 75%. Trimethyl boron is slowly separated on heating the mixture of trimethyl aluminum and tributyl boron up to the boiling point. The tributyl aluminum being produced contains up to 25% dibutyl aluminum hydride. In the interaction of tributyl boron with triethyl aluminum triethyl boron and also a mixture of tributyl aluminum and dibutyl aluminum hydride is formed which contains 50% of the latter.

Card 2/3

On the Reaction of Realkylation in the Aluminum and Boron SOV/62-59-1-37/38  
Trialkyl Series

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk  
SSSR( Institute of Elemental Organic Compounds of the Academy  
of Sciences, USSR)

SUBMITTED: September 9, 1958

Card 3/3

5(3)

AUTHOR: Zakharkin, L. I.

SOV/62-50-3-9/37

TITLE: Reaction Between 1,1-Dichlorohexene-1 and Sodium Ethyl Mercaptide (Deyatviye etilmerkaptida natriya na 1,1-dikhlorgeksen-1)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 3, pp 437-443 (USSR)

ABSTRACT: In the present paper the action exerted by sodium ethylmercaptide on 1,1-dichlorohexene-1 as well as on 1,2-dichlorohexene-1 and 1-chlorohexene-1 was investigated. On the heating of an alcoholic solution of sodium ethyl mercaptide with 1,1-dichlorohexene-1 2 compounds were obtained: 1-chloro-2-ethyl mercaptohexene-1 and 1,2-bis-(ethyl mercapto)-hexene-1. The same products were likewise obtained from 1,2-dichlorohexene-1 and 1-chlorohexene-1 under the action of ethyl mercaptide. Investigating the structure of these two compounds the following was found: On the action of 2,4-dinitro-phenyl hydrazine in the presence of sulphuric acid always the same 2,4-dinitro-phenyl hydrazone  $C_{14}H_{20}N_4O_4S$  is formed. On the heating of solutions of 1-chloro-2-ethyl mercapto hexene-1 and 1,2-bis-(ethyl mercapto)-hexene-1 in hydrochloric and acetic acid

Card 1/3

Reaction Between 1,1-Dichlorohexene-1 and Sodium  
Ethyl Mercaptide

SOV/62-59-3-9/37

mixture always the same 1-ethyl mercapto hexene-2 results. This yields the 2,4-dinitro-phenyl hydrazone which is identical with the 2,4-dinitro-phenyl hydrazone directly obtained from 1-chloro-2-ethyl mercapto hexene-1 and 1,2-bis-(ethyl mercapto)-hexene-1. As to the reaction of sodium ethyl mercaptide with 1,1-dichloro hexene-1 it may be assumed that the first reaction stage is the addition of  $C_2H_5SH$  to the dichloro vinyl group and the following separation of HCl. Apparently the separation of hydrogen chloride takes place more readily than the addition of ethyl mercaptane. Such an addition of ethyl mercaptane to the asymmetric dichloro vinyl group is in contradiction with the addition of a number of electrophilic reagents, if it proceeds by way of the addition of the  $C_2H_5S^-$ -anion. In the case of an action exerted by nucleophilic reagents on the dichloro vinyl group an induction effect of the chlorine atoms seems to occur which produces a fractional positive charge at the second carbon atom. The action of the nucleophilic reagents is directed to this carbon atom. In the case of electrophilic reagents,

Card 2/3

Reaction Between 1,1-Dichlorohexene-1 and Sodium  
Ethyl Mercaptide

SOV/62-59-3-9/37

however, the determinative direction appears to be the  
electromeric effect of chlorine atoms. It is not impossible  
that the addition of ethyl mercaptane takes place according  
to a radical mechanism although the reaction in the presence  
of diphenyl amine in nitrogen atmosphere offers the same  
results. There are 10 references, 4 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR  
(Institute of Elemental Organic Compounds of the Academy of  
Sciences, USSR)

SUBMITTED: June 11, 1957

Card 3/3



5(3)

AUTHORS:

Zakharkin, L. I., Savina, L. A.

SOV/62-59-3-10/37

TITLE:

Effect of Triethyl Aluminum and Diisobutyl Aluminumhydride on Some Allyl Compounds (Deystviye trietilalyuminiya i diizobutilalyuminygidrida na nekotoryye allil'nyye soyedineniya)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 3, pp 444-449 (USSR)

ABSTRACT:

In the present paper the effect of triethyl aluminum and diisobutyl aluminumhydride on allyl compounds  $\text{CH}_2=\text{CH}-\text{CH}_2\text{X}$ , X being OR, SR, and  $\text{NR}_2$ , was investigated. A cleavage of the C-X-bond takes place and an unsaturated hydrocarbon and corresponding  $(\text{C}_2\text{H}_5)_2\text{AlX}$  are formed. The inability of triethyl aluminum to react with the double bond of the allyl compounds investigated may be explained by the decreasing electron density at the heteroatom owing to the complex bond that reduces the activity of the double bond. In contrast with the triethyl aluminum the addition of the diisobutyl aluminumhydride to the double bond takes place comparatively easily.  $(i\text{-C}_4\text{H}_9)_2\text{-AlCH}_2\text{CH}_2\text{CH}_2\text{X}$  are formed herein, where X = OR,  $\text{NR}_2$ ,

Card 1/2

Effect of Triethyl Aluminum and Diisobutyl Aluminum- SOV/62-59-3-10/37  
hydride on Some Allyl Compounds

and SR. Further an attempt was made to allow the diisobutyl aluminumhydride to react with the double bond of the vinyl butyl ether. As a result of this reaction which proceeds with self-heating, ethylene (already at 30-35°) and butoxy diisobutyl aluminum were obtained. Apparently the organic aluminum compound of the  $R_2Al-CH_2CH_2OR$  type, which is initially formed, is as unstable as similar organic magnesium compounds  $XMgCH_2CH_2X$  (Refs 6,7). It decomposes, while ethylene is eliminated and alcoholate  $(i-C_4H_9)_2AlH + CH_2=CH-OC_4H_9 \longrightarrow (i-C_4H_9)_2AlCH_2CH_2OC_4H_9 \longrightarrow (i-C_4H_9)_2AlOC_4H_9 + CH_2=CH_2$  is formed. There are 12 references, 1 of which is Soviet.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR  
(Institute of Elemental Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: June 14, 1957  
Card 2/2

5(3)

AUTPORS:

Zakharkin, L. I., Khorlina, I. M.

SOV/62-59-3-27/37

TITLE:

Thermal Decomposition of Adducts of Diisobutyl Aluminum Hydride on Nitriles (Termicheskoye razlozheniye produktov prisoyedineniya diizobutilalyuminiygidrida k nitrilam)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 3, pp 550-552 (USSR)

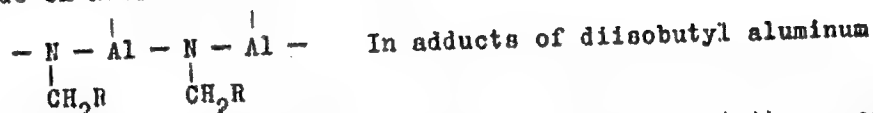
ABSTRACT:

In the preceding paper (Ref 1) the authors obtained the adducts of diisobutyl aluminum hydride and the nitriles  $RCH=N-Al(i-C_4H_9)_2$ . In the present paper the behavior of these products was investigated when they are heated. It was found that a gas consisting mainly of isobutylene is separated if the compounds  $RCH=N-Al(i-C_4H_9)_2$  are heated to temperatures of from 220-240°. In the hydrolysis of the residue, however, the corresponding amine  $RCH_2NH_2$  forms with a yield of up to 80 % of the theoretically computed value. Thus, in heating a reduction takes place due to the displacement of isobutylene and the formation of new Al-N bonds. In this reduction products of the following linkage systems form:

Card 1/2

Thermal Decomposition of Adducts of Diisobutyl  
Aluminum Hydride on Nitriles

SOV/62-59-3-27/37



hydride and disubstituted amides a reduction at the expense of the displacement of isobutylene is possible in principal. It is, however, only unimportant and furthermore, is accompanied by strong resinification. There are 8 references, 1 of which in Soviet.

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk SSSR  
(Institute of Elemental Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: July 16, 1958

Card 2/2

SOV/62-59-5-32/40

5(3)

AUTHORS:

Zakharkin, L. I., Sorokina, L. P.

TITLE:

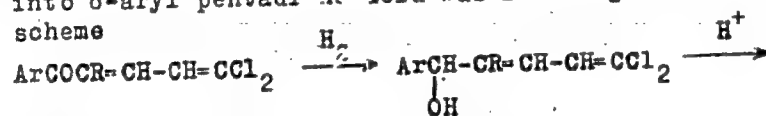
Rearrangement of 1,1-Dichloro-5-oxo-(Chloro)-5-aryl pentadienes-1,3 Into  $\delta$ -Arylpentadiene Acids (Peregruppirovka 1,1-dikhlor-5-oksi (khlor)-5-arilpentadiyenov-1,3 v  $\delta$ -arilpentadiyenovyye kisloty)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 5, pp 936-938 (USSR)

ABSTRACT:

In the present paper the reduction of some 1,1-dichloro-5-oxo-5-phenyl pentadienes-1,3 into the corresponding oxide derivatives was carried out, and the allyl-anionotropic isomerization into  $\delta$ -aryl pentadiene acid was investigated according to the scheme



$\text{ArCH}=\text{CR}-\text{CH}=\text{CH}-\text{COOH}$ . Such a re-grouping in pentadienes has hitherto not been investigated. The reduction of the following diene ketones was carried out with aluminum isopropylate in isopropyl alcohol:  $\text{ArCOCR}=\text{CH}-\text{CH}=\text{CCl}_2$  with 1)  $\text{Ar} = \text{C}_6\text{H}_5$ ,  $\text{R} = \text{H}$ ;

Card 1/2

S07/62-59-5-32/40

Rearrangement of 1,1-Dichloro-5-oxy (Chloro)-5-arylpentadienes-1,3 Into  
o-Arylpentadiene Acids

2) Ar = C<sub>6</sub>H<sub>5</sub>, R = CH<sub>3</sub>; 3) Ar = p-ClC<sub>6</sub>H<sub>4</sub>, R = H. Of these three  
oxide derivatives obtained only 1,1-dichloro-5-oxy-4-methyl-5-  
phenylpentadiene-1,3 showed sufficient resistance to heat, so  
that it could be distilled without being changed. The other  
two alcohols had to be converted into the corresponding  
chlorides for the purpose of vacuum distillation. In the ex-  
perimental the individual reactions are described and the  
physical characteristics of the substances obtained are given.  
There are 5 references, 2 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR  
(Institut of Elemental-organic Compounds of the Academy of  
Sciences, USSR)

SUBMITTED: October 24, 1958

Card 2/2

5 (3)

AUTHORS:

Zakharkin, L. I., Gavrilenko, V. V.

SOV/62-59-8-39/42

TITLE:

Anomalous Reaction Course in the Displacement of Isobutylene by Means of Styrene From Triisobutylaluminum

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 8, p 1507 (USSR)

ABSTRACT:

In the displacement reaction of triisobutylaluminum and styrene an affiliation of aluminum to both the first and second carbon atom could be observed contrary to Ziegler's statements (Refs 1, 2). The two isomers were obtained in a ratio ~ 7:3. The following equation is given for the reaction:  $C_6H_5CH=CH_2 + i-C_4H_9Al \rightarrow C_6H_5CH(CH_3)-Al + C_6H_5CH_2CH_2-Al + i-C_4H_8$ ,  $Al = 1/3 Al$ . After the

oxidation of the obtained mixture with chromic anhydride in acetic acid, acetophenone and phenyl acetic acid were precipitated under the influence of carbon dioxide-ethylbenzoic and cinnamic acid. Similar results were obtained in the investigation of the affiliation of diisobutylaluminum to styrene. There are 2 references.

Card 1/2

Anomalous Reaction Course in the Displacement of  
Isobutylene by Means of Styrene From Triisobutylaluminum

SOV/62-59-8-39/42

ASSOCIATION: Institut elementorganicheskikh soedineniy Akademii nauk SSSR  
(Institute of Elemental-organic Compounds, Academy of Sciences,  
USSR)

SUBMITTED: May 22, 1959

Card 2/2



5.3610

77071  
SOV/62-59-12-15/43

AUTHORS: Zakharkin, L. I., Khorlina, I. M.  
TITLE: Reduction of Substituted Amides to Aldehydes and  
Amines With Diisobutylaluminum Hydride  
PERIODICAL: Izvestiya Akademii nauk SSSR. Otdelenie khimicheskikh  
nauk, 1959, Nr 12, pp 2145-2150 (USSR)  
ABSTRACT: Dialkylamides of aliphatic acids and amides of aromatic  
acids are reduced with diisobutylaluminum hydride. The  
yields of aldehydes are given in Table 1. The yields  
of amines obtained by reduction of mono- and disubsti-  
tuted amides with  $(i\text{-C}_4\text{H}_9)_2\text{AlH}$  are given in Table 2.

Card 1/5

Reduction of Substituted Amides to  
Aldehydes and Amines With Diisobutylaluminum  
Hydride

77071  
SOV/62-59-12-15/43

REDUCTION TO ALDEHYDES

(TEMP 0°; RATIO AMIDE TO HYDRIDE 1:1.5)

**TABLE 1**

AMIDES	FIELD OF ALDE- HYDES (%)	mp of 2,4-dinitrophenyl- hydrazones in °C	
		FOUND	ACC. TO LITERATURE
1 ETHANILAMIDE OF BUTYRIC ACID	1	56	122
2 DIMETHYLAMIDE OF ISOVALERIC ACID	2	25	117
3 ETHANILAMIDE OF ISO VALERIC ACID	3	52	116-117
4 DIMETHYLAMIDE OF EVANTHIC ACID	4	30	117
5 ETHANILAMIDE OF EVANTHIC ACID	5	50	106,5-107
6 DIMETHYLAMIDE OF CAPRYLIC ACID	6	28	197
7 ETHANILAMIDE OF CAPRYLIC ACID	7	50	106,5-107
8 DIMETHYLAMIDE OF CAPRYLIC ACID	8	52	100
9 ETHANILAMIDE OF CAPRYLIC ACID	9	44	101
10 DIMETHYLAMIDE OF BENZOIC ACID	10	48	103
11 ETHANILAMIDE OF BENZOIC ACID	11	67	103
12 DIMETHYLAMIDE OF BENZOIC ACID	12	70	210-217
13 ETHANILAMIDE OF BENZOIC ACID	13	44	210-217
14 DIMETHYLAMIDE OF NICOTINIC ACID	14	53	216-217
15 ETHANILAMIDE OF NICOTINIC ACID	15	60	236-247
16 DIMETHYLAMIDE OF AZELAIC ACID	16	54	239,5
17 ETHANILAMIDE OF 6-PHTHALIC ACID	17	30	111-142
18 DIMETHYLAMIDE OF OLEIC ACID	18	60	280
19 ETHANILAMIDE OF 6-ARABOBENZOIC ACID	19	60	280
20 DIMETHYLAMIDE OF ANISIC ACID	20	50	67-68
21 ETHANILAMIDE OF PHENYLACETIC ACID	21	50	190-190,5
			254
			110

Card 2/5

Reduction of Substituted Amides to  
Aldehydes and Amines With Diisobutylaluminum  
Hydride

77071  
SOV/62-59-12-15/43

TABLE 2

REDUCTION OF AMIDES TO AMINES					
AMIDE	RATIO OF AMIDE TO ( $\text{C}_4\text{H}_9$ ) <sub>2</sub> AlH	YIELD OF AMINE (%)	mp of derivatives in °C		
			FOUND	lit. to	LITERATURE
1 DIETHYL BENZAMIDE	1:1:2,2	75	120 a)	120	
2 "	1:1:2,5	79	120	120	
3 "	1:1:3	91	120	120	
4 DIMETHYLBENZAMIDE	1:1:3	93	175	175	
5 DIETHYLAMIDE OF ACETIC ACID	1:1:3	90	184,5 b	185	
6 DIETHYLAMIDE OF ISOBUTYRIC ACID	1:1:2,5	80	132 a)	132	
7 "	1:1:3	95	132	132	
8 DIMETHYLAMIDE OF ENANTHIC ACID	1:1:3	91	83 a)	83	
9 DIMETHYLAMIDE OF CAPROIC ACID	1:1:3	93	65 a)	62-65	
10 CAPROLACTAM	1:1:4	95	145 a)	146	
11 ISOBORNYL BENZAMIDE	1:1:4	95	c)	*	

a -- picrate; b -- dihydrochloride; c -- hydrochloride

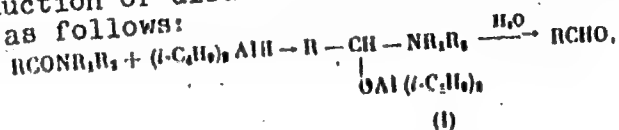
\* Found for isobornylbenzylamine: 01 12.47

Card 3/5

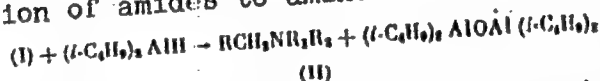
Reduction of Substituted Amides to Aldehydes and Amines With Diisobutylaluminum Hydride

77071  
SOV/62-59-12-15/43

The reduction of disubstituted amides to aldehydes occurs as follows:



The reduction of amides to amines occurs according to scheme:



There are 5 tables; and 21 references, 1 Soviet, 5 German, 3 French, 5 U.S., 7 U.K. The 5 most recent U.S. and U.K. references are: V. M. Micovic, M. L. Mihailovic, J. Org. Chem., 18, 1190 (1953); O. D. Johnson, J. Am. Chem. Soc., 48, 7543 (1954); E. A. Braude, R. U. Jones, J. Chem. Soc., 498 (1943); J. D. Roberts, Ch. Green, J. Am. Chem. Soc., 68, 214 (1946); R. E. Benson, F. L. Cairus, J. Am. Chem. Soc. 70, 2115 (1948).

Card 4/5

Reduction of Substituted Amides to  
Aldehydes and Amines With Diisobutylaluminum  
Hydride

77071

SGV/62-59-12-15/43

ASSOCIATION: Institute of Elementoorganic Compounds, Academy of  
Sciences USSR (Institut elementoorganicheskikh  
soedineniy, Akademii nauk SSSR)

SUBMITTED: April 18, 1958

Card 5/5

ZAKHARKIN, I. M.

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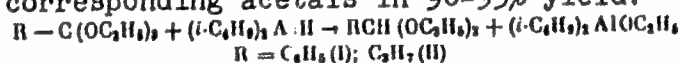
77096  
SOV/62-59-12-40/43

AUTHORS: Zakharkin, L. I., I. M. KHORLINA

TITLE: Hydrogenolysis of C-O Bond in Ortho-Esters, Acetals, and Some Ethers by the Action of Diisobutylaluminum Hydride. Brief Communications

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 12, pp 2255-2257 (USSR)

ABSTRACT: The C-O bond in ortho-esters (I) and (II) was easily hydrogenolized on heating at 300° with diisobutylaluminum hydride in dry benzene. The reaction gave the corresponding acetals in 90-95% yield.



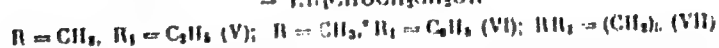
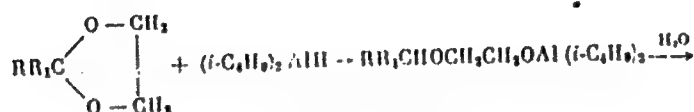
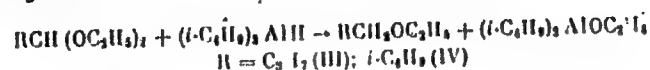
Diisobutylaluminum hydride also easily hydrogenolized (at 70-80°) diacetals (III) and (IV) as well as ketals (V), (VI), and (VII), giving the corresponding ethers in 80-90% yield:

Card 1/3

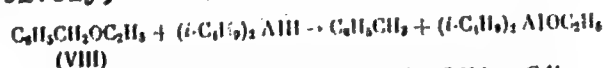
Hydrogenolysis of C-O Bond in Ortho-Esters,  
Acetals, and Some Ethers by the Action of  
Diisobutylaluminum Hydride. Brief Communications

77096

SOV/62-59-12-40/43



It was also shown that the ether bond was easily hydrogenolized by diisobutylaluminum hydride on heating at 120-140°. Ethyl benzyl ether (VIII) and ethyl phenyl ether (IX) gave toluene and ethane, respectively, in 87-92% yield.



Card 2/3

Hydrogenolysis of C-O Bond in Ortho-Esters,  
Acetals, and Some Ethers by the Action of  
Diisobutylaluminum Hydride. Brief Communications

77096

SOV/62-59-12-40/43

Diisobutylaluminum hydride can be used, therefore, in cases where lithium aluminum hydride was ineffective, as in hydrogenolysis of acetals, ketals, and ethers. There are 14 references, 9 U.S., 1 U.K., 1 French, 3 German. The 5 most recent U.S. and U.K. references are: B. R. Brown, C. A. Somersfield, Proc. Chem. Soc., 1958, 7; E. L. Ellel, M. Rerick, J. Org. Chem., 23, 1088 (1958); W. E. Parhan, H. Wynberg, F. L. Pamp, J. Amer. Chem. Soc., 75, 2065 (1953); W. Oroshnik, A. D. Mebane, G. Karmas, ibid., 75, 1053 (1953); H. M. Donkas, T. D. Fontaine, ibid., 75, 5355 (1953).

ASSOCIATION: Institute of Element-Organic Compounds, Academy of Sciences, USSR (Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)

SUBMITTED: May 22, 1959

Card 3/3



5 (3)

AUTHORS:

Samokhvalov, G. I., Zakharkin, L. I., SOV/20-126-5-28/69  
Davydova, L. P., Khorlina, I. M.

TITLE:

A New Synthesis of  $\beta$ -Ionolidenacetic Aldehyde (Novyy sintez  $\beta$ -ionolidenuksusnogo al'degida)

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol. 126, Nr 5, pp 1013 - 1016 (USSR)

ABSTRACT:

"9,13 dimethyl-7-(1,1,5 trimethyl-cyclohexene-5-yl)-octatriene 8,10,12 al 14; aldehyde C<sub>19</sub> (I)" is an intermediate product of the  $\beta$ -carotene synthesis (Ref 1). The extension of the carbon chain of this compound by one atom and the creation of a conjugate system of double bonds renders the transition to stereo-isomeric retinal aldehydes possible, which corresponds to the vitamin A. The above mentioned chain-extension is based on the formation of cyanohydrins (Refs 2,3). For the reduction of the nitriles, arising after the dehydration, di-isobutyl-aluminum hydride (Ref 4) could be used. The authors describe a realisation of this method with reference to a simple example: The synthesis mentioned in the title (Ref 5) of 7-(1,1,5 trimethyl-cyclohexene-5-yl)-9-methyl butene-8-al-10 of  $\beta$ -C<sub>14</sub> al-

Card 1/3

A New Synthesis of  $\beta$ -Ionolidenacetic Aldehyde

SOV/20-126-5-28/69

dehyde (II) (see scheme). The interaction between aldehyde C<sub>11</sub> (II) with acetone-cyanhydrine takes place under the influence of a methanol solution of potash at 20-23°. The oxy-nitrile yield (III) amounts to 83-84%. By the reduction of the nitrile- $\beta$ -ionolide-acetic-acid (Fig 1) (IV) the substance mentioned in the title (V) was produced as a stereo-isomeric mixture, and was isolated. In the crystallization of the semi-carbazones of the stereo-isomeric-aldehydes from alcohol trans- $\beta$ -ionolide acetic aldehyde semi-carbazone was obtained (melting point 195.5°-196° Refs 7,8), and a far smaller quantity of the cis-isomers (melting point 173-174°). A far-reaching agreement of the maxima of the ultra-violet absorption spectra of the carbazones of the isomeric aldehydes (Fig 2) allows the conclusion that the isomery is caused by a deviation of the position of the substituents with regard to the newly formed, sterically not impeded, double-bond of the carbon atoms 9-10. Out of the carbazone of the trans- $\beta$ -ionolide-acetic aldehyde free aldehyde was obtained. The infrared spectrum (Fig 3) is characteristic of substances with a trans-position of the substituents at the double bond. Bands in the range of 6.25 $\mu$  belong to the

Card 2/3

A New Synthesis of  $\beta$ -Ionolidenacetic Aldehyde

SOV/20-126-5-28/69

oscillations of the system of conjugate double bonds, whilst those at  $6\mu$  correspond to the  $\nu$ -oscillation  $C=O$  in the system with conjugate unsaturated bonds. Prof. N. A. Preobrazhenskiy showed interest in this investigation. There are 3 figures and 8 references, 2 of which are Soviet.

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Card 3/3

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